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(54) Title: PROCESS FOR TREATMENT OF UNDERGROUND RESERVOIRS

(57) Abstract: A process for treating an underground reservoir, which process comprises (a) introducing into the reservoir, separately or together: (i) and ester, and (ii) a compound containing at least one carboxylae functionality, the compound being water-soluble and capable of increasing the rate of hydrolysis of the ester; each of components (i) and (ii) being contained in a treatment fluid in which it is dissolved or dispersed in water; and (b) allowing the ester to hydrolyse to produce an organic acid in an amount effective to acidise the underground reservoir.

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# PROCESS FOR TREATMENT OF UNDERGROUND RESERVOIRS

The process of the present invention is generally applicable to the production of oil, gas or water from wells drilled into underground reservoirs.

During drilling, workover and production operations there are numerous situations where the production rate of an oil, gas or water well following these operations is limited due to the presence of formation damage. Types of damage include, but are not limited to, the presence of polymer-containing filter cakes including drilling mud filter cakes, fluids (including hydraulic fracturing fluids) filtrates or residues including polysaccharide-containing filter cakes, fluids, filtrates or residues; particulate materials such as fluid loss control agents, bridging agents and rock fines, biofilms, scales and asphaltenes. Damage may arise as a result of drilling, production, injection, workover or other oilfield operations.

Damage can be near wellbore, for example the presence of drilling mud or fracturing fluid filter cake, or damage may be present deeper into the formation, for example mineral scale deposited in natural or induced fractures or in the rock matrix.

The effective removal of damage, especially near wellbore damage such as filter cake, can significantly increase the production rate of hydrocarbon or water producing wells penetrating underground formations. The effective removal of damage can also increase the injectivity of injection wells.

Treatment with acid (acidizing) has been used for many years to treat damage in underground formations and stimulate the rate of oil or gas production.

If acids can be delivered sufficiently well into the formation, acidising may also be effective in stimulating undamaged formations, particularly carbonate formations, by

increasing the permeability of the rock matrix around the wellbore. For example, increasing the permeability of a radial zone around a vertical or other wellbore will increase the rate of fluids production (or injection rate) in a situation where there is no near wellbore damage. The efficient delivery of acids into fractures such as induced fractures or natural fractures or natural fracture networks can also increase the conductivity of the fractures allowing higher rates of fluid production or injection.

Acids may also be used to break acid-sensitive gels such as crosslinked guar-borate gels used in hydraulic fracturing and other oilfield applications. Efficient breaking of gels is generally required to obtain maximum production after such treatments. Acid may also be used to break mixed metal hydroxides or complexes of mixed metal hydroxides with materials such as bentonite.

However, conventional acids have several drawbacks. They react rapidly with acid soluble materials which can prevent effective placement of reactive acid deep into carbonate formations or throughout long horizontal wellbores resulting in poor zonal coverage. These acids are also hazardous in use. To improve zonal coverage the use of high pressure, high rate injection is often attempted, which increases the hazards associated with their use of conventional acids .

One approach which can improve zonal coverage has been the use of solutions of carboxylic acid esters which hydrolyse at high temperatures to produce a carboxylic acid downhole (US 3,630,285). Preferably, the formation temperature for this process is greater than about 150°C. Because the acid is produced predominantly after placement of the fluid improved zonal coverage can be achieved. The preferred esters used in US 3,630,285 were ethyl acetate and methyl formate. These compounds have the disadvantage of low flash points and have other health and safety drawbacks such as some degree of toxicity.

US 3,630,285 indicates that ester hydrolysis generally proceeds too slowly. It considers the possible use of strong acids and alkalis to increase the rate of hydrolysis of the esters, but then discounts the use of such catalysts downhole, due to the fact that carbonate (limestone) formations will rapidly neutralise the catalytic effects of these materials.

US 5,678,632 teaches the use of enzymes to increase the rate of hydrolysis of esters, providing a highly effective means of generating carboxylic acids *in-situ* for acidizing without using extremes of pH and extending the range of downhole temperatures over which useful rates of hydrolysis of esters can be obtained. The use of certain types of non-enzyme catalysts to increase the rate of hydrolysis of esters and achieve effective acidizing has been taught in WO 01/02698. Non-enzyme catalysts taught included metal ions such as transition metal ions, organic molecules including amino acids, peptides, monosaccharides, oligosaccharides, nucleic acids, peptide nucleic acids and derivatives of organic molecules and combinations thereof.

The enzymes and non-enzyme catalysts of US 5,678,632 and WO 01/02698 are typically used at relatively low concentrations of up to a few percent v/v enzyme concentration or 1 to 10 mM non-enzyme catalyst. The solution containing the ester and enzyme or non-enzyme catalyst is made up in a suitable aqueous fluid such as fresh water, produced water or seawater.

It is an object of the present invention to provide further simple and effective processes for increasing the rate of hydrolysis of esters to facilitate ester based acidizing of underground formations. It is a further object of the present invention to provide simple and effective processes for acidising underground formations in combination with one or more polymer breakers, where desired. It is also an object of the present invention to provide a process by which increased rates of ester hydrolysis can be obtained in fluids over a wide density range, including high density (heavy) brines. Aditionally, the present invention provides processes and chemicals

that are generally low hazard and environmentally acceptable.

It has unexpectedly been found that certain compounds containing a carboxylate functionality when mixed in a suitable concentration range with suitable esters, usefully increase the rate of hydrolysis of the esters and form the basis of a novel and effective acidizing process. In common with the processes of US 5,678,632 and WO 01/02698 this process may be used to achieve acidizing at a predictable rate with excellent zonal coverage.

Accordingly, the present invention provides a process for treating an underground reservoir, which process comprises

(a) introducing into the reservoir, separately or together:
   (i) an ester, and
   (ii) a compound containing at least one carboxylate functionality, the compound being water-soluble and capable of increasing the rate of hydrolysis of the ester;
   each of components (i) and (ii) being contained in a treatment fluid in which it is dissolved or dispersed in water; and
(b) allowing the ester to hydrolyse to produce an organic acid in an amount effective to acidise the underground reservoir.

The process of the present invention aims to achieve controlled and effective acidizing for purposes such as increasing the rate of production (or injection) of wells drilled into the formation, increasing the permeability of the formation, for example the permeability of the rock matrix or of induced or natural fractures or fracture networks, treating filter cake, including following a gravel packing operation, and treating a biofilm.

The acid produced by the process of the present invention may dissolve acid soluble material such as calcium carbonate and other carbonates. It may also be used to

break acid-sensitive gels such as crosslinked guar-borate gels used in hydraulic fracturing and other oilfield applications or to disrupt acid sensitive materials such as mixed metal hydroxides and complexes of mixed metal hydroxides with materials such as bentonite. The process may also be used in any other downhole application where the in-situ production of acid may be useful.

Optionally, the process of the present invention allows controlled acidising in combination with suitable polymer breakers. Polymer breakers may be selected where polymers or gels are present in the formation, for example in filter cakes or fracturing, completion or workover fluids.

Where the process of the present invention is used to treat filter cakes following gravel packing operations, the treatment fluid may be used as the base fluid for gravel packing or be introduced after gravel packing.

The reservoir may be a hydrocarbon reservoir, for instance a gas or oil reservoir. Alternatively the reservoir may be a water reservoir. When it is a hydrocarbon reservoir the process of the invention may further include recovering a hydrocarbon from the treated reservoir. Likewise, when it is a water reservoir the process of the invention may further include recovering water from the treated reservoir. Typically the reservoir is, or includes, carbonate or sandstone rock structures.

Preferred esters for use as component (i) in the process of the present invention as defined above are carboxylic acid esters, preferably those with low toxicity, high flash point and high environmental acceptability. Esters of ethanoic and methanoic acid (acetic and formic acid) are particularly suitable. The calcium and magnesium salts of these acids have good solubility in water, formate brines, acetate brines and many other brines, which is advantageous when the acid produced by the process of the present invention is used to dissolve calcium carbonate, magnesium carbonate, calcium magnesium carbonate (dolomite) or other acid soluble calcium or

magnesium salts.

The ester should be at least slightly water soluble. Preferably the ester should be soluble to at least 1% w/v in water and most preferably soluble to at least 5% w/v in water. Preferably 5% to 20% w/v ester will be used but concentrations of ester higher than 20% w/v may be used in some cases. In general it has been found that 5% to 10% w/v ester is sufficient to give good increases in permeability or good removal of filter cake damage. The solubility of some esters may be reduced in high salt concentration fluids such as heavy brines, compared to their solubility in water. In such cases an ester which is completely soluble in the base fluid to a sufficient concentration will normally be selected. In some situations, it may be desirable or necessary to use an emulsion of an ester in the treatment fluid.

The alcohol portion of the ester may be monohydric or polyhydric as long as the esters are sufficiently water soluble at formation temperatures. Partial esters of the polyhydric alcohols can be used in which case the unesterified hydroxyl groups serve to increase the water solubility of the ester.

Examples of suitable esters include acetic and formic esters of 1,2,3-propanetriol ethylene glycol diethylene glycol and triethylene glycol. Most preferably the esters are acetic esters of 1,2,3-propanetriol (glycerol) and 1,2-ethanediol (ethylene glycol) diethylene glycol and triethylene glycol. The ester and also the alcohol which is produced when the ester hydrolyses can both act as mutual solvents. The presence of a mutual solvent is generally considered to be beneficial in treatments of hydrocarbon bearing formations, particularly when treating with water based treatment fluids.

Any compound which contains at least one carboxylate function (i.e. -COO), and which is both water-soluble and capable of increasing the rate of hydrolysis of the ester, may be used as component (ii) in the process of the present invention. Suitable such compounds can be readily selected by a person of skill in the art. In general the

compounds will be selected on the basis of their effectiveness at increasing the rate of hydrolysis of the preferred esters under the required conditions, their cost and their environmental and operational acceptability.

Component (ii) is generally a salt of a mono-, di- or poly-carboxylic acid. Typically the carboxylic acid is an aliphatic carboxylic acid. Examples of suitable salts include salts of a carboxylic acid of formula $RCO_2H$ wherein R is selected from hydrogen, an alkyl group having from 1 to 6 carbon atoms and $-R'CO_2H$ where R' is a bond or an alkylene group having from 1 to 6 carbon atoms, the said alkyl or alkylene group being branched or unbranched and unsubstituted or substituted. Suitable examples of substituent groups include halogen, hydroxy, $C_1$-$C_6$ alkoxy, SH, amino, nitro, cyano and phenyl. Preferred examples of component (ii) are salts of formic acid, acetic acid, hydroxyacetic acid, malonic acid, succinic acid, oxalic acid and citric acid.

Component (ii) may alternatively be a salt of a chelating compound which includes at least one carboxylate functionality. Examples include salts of ethylenediamine tetraacetic acid (EDTA) and nitrilotriacetic acid (NTA).

The preferred salts for use as component (ii) are salts with alkali metal (i.e.Periodic Table group I) metal cations, such as sodium, potassium or caesium, and alkaline earth metal (Periodic Table group II) cations such as magnesium and calcium. Particularly preferred are alkali metal carboxylates and alkaline earth metal carboxylates, particularly the salts of alkali metals or alkaline earth metals with formic acid or acetic acid. Especially preferred are potassium formate, potassium acetate, sodium formate, sodium acetate, caesium formate, caesium acetate, magnesium formate, magnesium acetate, calcium formate and calcium acetate. Weak base salts of acetic acid and formic acid, for instance the ammonium and amine salts, are also suitable.

In a preferred embodiment the present invention therefore provides a process for treating an underground reservoir, which process comprises introducing into the reservoir a treatment fluid which comprises, dissolved or dispersed in water, an ester and a carboxylic acid salt, such that the ester hydrolyses to produce an organic acid to dissolve acid soluble material present within the reservoir, the salt being water-soluble and capable of increasing the rate of hydrolysis of the ester.

Component (ii) is typically incorporated into the treatment fluid at a concentration sufficient to increase the rate of ester hydrolysis, by at least several tens of percent and preferably by a factor of at least double the rate of hydrolysis of the ester at the same temperature in the absence of the carboxylic acid salt. Concentrations of the carboxylic acid salt of at least 5% w/v and preferably 10% to 75% weight/volume are generally used, although higher or lower concentrations may be used if they accelerate the rate of ester hydrolysis to the desired degree. The maximum concentration of a given carboxylic acid salt which may be used in a treatment fluid varies according to the solubility of the specific salt in the treatment fluid formulation. In some circumstances, for example where significant dilution of the treatment fluid is expected to occur downhole, saturated solutions of the carboxylic acid salts containing solid salt could be used.

To achieve a treatment fluid of the desired density component (ii) may, if required, be blended with other salts or salt solutions as long as the blended fluid retains the ability to increase the rate of hydrolysis of the ester and there is no incompatibility. Suitable other salts or salt solutions include any brine which may be used in the oilfield including but not being limited to sodium chloride, sodium bromide, potassium chloride, potassium bromide, potassium formate, calcium chloride, calcium bromide, zinc chloride, zinc bromide caesium formate and caesium tungstate which may be used in drilling, completion and workover operations.

The acid generated from component (i) in the process of the present invention is an

organic acid, generally an aliphatic carboxylic acid. Preferably the acid is of formula $RCO_2H$ wherein R is selected from hydrogen, an alkyl group having from 1 to 6 carbon atoms and $-R'-CO_2H$ where R' is a bond or an alkylene group having from 1 to 6 carbon atoms, the said alkyl or alkylene group being branched or unbranched and unsubstituted or substituted. Suitable examples of substituent groups include halogen, hydroxy, $C_1$-$C_6$ alkoxy, SH, amino, nitro, cyano and phenyl. The most preferred aliphatic carboxylic acids are acetic acid and formic acid. Where the acid has a hydroxy substituent the ester may, for instance, be a cyclic ester such as a lactone.

Components (i) and (ii) need to be retained in the underground reservoir for a period which is long enough for the desired amount of acid to be produced. The or each treatment fluid used to deliver these components in the process of the present invention will normally require shut in periods between 2 hours and 2 weeks, preferably 24 hours to 1 week depending on the application and downhole conditions although shorter or longer shut in periods may also be appropriate in some situations. The desired treatment period will be readily determined by one skilled in the art. .

In addition to the preferred esters which would normally comprise the majority of the esters present in the treatment fluids used in the current invention, it may also be beneficial in some damage removal applications to include in the formulation esters of chelating compounds such as malonic acid, oxalic acid or succinic acid (US 5,082,056) ethylenediaminetetraacetic acid (EDTA) nitrilotriacetic (NTA) citric acid or hydroxyacetic acid (US 5,223,159) which on hydrolysis produce efficient chelating compounds. Such compounds may be particularly useful to assist in the breaking of cross-linked polymers in may be used in combination with other polymer breakers. Some of the acids produced from the hydrolysis of the ester may be able to dissolve certain types of oilfield scale. For example hydroxyacetic acid can dissolve calcium sulphate.

Although the process of the present invention uses a compound which contains a carboxylate functionality to increase the rate of hydrolysis of suitable esters, there may be circumstances in which such compounds are used in combination with enzyme or non-enzyme catalysts that can also increase the rate of hydrolysis of the esters.

In one embodiment of the invention the or each treatment fluid further includes one or more polymer breakers to degrade polymers, normally polysaccharide polymers. Alternatively the polymer breaker may be formulated in a separate treatment fluid. Preferred polymer breakers for use in the process of the present invention are oxidants (oxidative breakers) and enzyme breakers. A polymer breaker component (iii) may thus be introduced into the reservoir in an amount effective to degrade polymers present within the reservoir. It is introduced either together with or separately from one or both of components (i) and (ii).

Oxidative breakers used in the present invention may be any one of those oxidative breakers known in the art to be useful to react with polymers to reduce the viscosity of polymer thickened compositions or to disrupt filter cakes. The oxidative breaker is typically introduced in a treatment fluid containing the ester component. The oxidative breaker may be present in solution or as a dispersion. Suitable compounds include persulphates, peroxides, perborates, percarbonates, perphosphates, hypochlorites, persilicates, metal cations and hydrogen peroxide adducts such as urea hydrogen peroxide and magnesium peroxide.

Preferred oxidative breakers for incorporation into treatment fluids to be used in the present invention are peroxides which can decompose to generate hydrogen peroxide. Of the oxidative breakers most preferred are percarbonates and perborates, most especially sodium percarbonate and sodium perborate.

Preferred polymer breaking enzymes used in the present invention include hydrolases and lysases, such as any one of those polysaccharide degrading enzymes known in the art to be useful to degrade (normally hydrolyse) polysaccharides and to reduce the viscosity of polysaccharide thickened compositions or to disrupt filter cakes. The polymer breaking enzymes will be selected on the basis of their known ability to hydrolyse the polysaccharide components known or believed to be contributing to the damage. Examples of suitable enzymes which may be used to break polymers include enzymes which can hydrolyse starch, xanthan, cellulose, guar, scleroglucan, succinoglycan or derivatives of these polymers.
If suitable enzyme activities are available, enzymes could also be used to hydrolyse any other polymers suitable for use in drilling, workover or production operations. Appropriate enzymes for this purpose are well documented in the literature and would be well known to a person of skill in the art.

Oxidative or enzyme breakers or catalysts capable of hydrolysing other, non-polysaccharide polymers may also be incorporated into treatment fluids used in the present invention.

Where a breaker is incorporated into a treatment fluid to be used in the process of the present invention, sufficient polymer breaker or gel breaker is normally included to have a substantive effect on the polymer component. The concentration of polymer breaker incorporated into the formulation will vary according to the type of breaker employed, the nature of the polymer and its concentration in the base fluid but will be of the order of 0.005 to 60 kg / $m^3$, preferably 0.2 to 10 kg / $m^3$.

In general it is desirable to use a concentration of breaker that results in the breaking of the polymer over a period of several hours to allow the effective placement of the treatment fluid. For example, too rapid a degradation of a filter cake or biofilm may lead to early localised fluid leak off, adversely affecting placement of the remaining treatment fluid. This is analogous to the situation experienced in treatments using

conventional acids, where the fast reaction rate can result in rapid breakthrough and wormholing and uneven fluid leak off. This can prevent the even placement of fluid containing conventional acids over long horizontal intervals or into fractures or the rock matrix.

It is a feature of the process of the present invention that use of an ester rather than a reactive acid avoids wormholing and improves the placement of the fluid. In order to maintain this advantage in certain applications such as the treatment of long horizontal intervals, too rapid a degradation of polymers in for example filter cakes or biofilms should in general be avoided. Ideally, breakthrough of filter cakes or biofilms will be achieved after a period longer than that amount of time needed to place a treatment fluid throughout the zone requiring treatment. A delay in producing a substantive amount of acid and in breaking polymer allows even treatment of the target zone and excellent zonal coverage.

Use of an ester rather than a reactive acid gives the advantages described in US 3,630,285 and US 5,678,632 with respect to effective placement of the fluid. Where suitable esters are selected, in particular where low toxicity, high flash point esters are used, there are also health and safety and environmental advantages. The initially near neutral or alkaline pH of the treatment fluids permits the incorporation of acid incompatible gel breakers such as enzymes and oxidative breakers into the fluid without the compatibility problems encountered when such breakers are incorporated into highly acidic formulations based on mineral or organic acids.

Enzymes useful as polysaccharide breakers in the process of the present invention will generally be selected to have activity in the same pH range as the treatment fluid. The generation of carboxylic acid by the hydrolysis of esters in the presence of carboxylate-containing compounds such as carboxylic acid salts, and acid soluble material such as calcium or magnesium carbonates, produces a relatively strongly buffered system wherein the pH does not shift by more than a few pH units as acid is

produced. The activity of polysaccharide breaking enzymes in a given treatment fluid formulation can therefore be readily predicted.

In some embodiments of the present invention, the effectiveness of the incorporated oxidant breakers can be enhanced by producing more reactive oxidants. Specifically, under certain conditions the production of hydrogen peroxide in the presence of organic acid can result in the formation of a peracid which is a more effective oxidant than the hydrogen peroxide. Thus, in one embodiment of the process of the invention the treatment fluid further comprises a peroxide to generate a peracid polymer breaker *in situ*.

The ester, the compound containing a carboxylate functionality and other chemicals required for the process of the present invention will normally be technical grade to reduce the cost of the process.

Where an enzyme is additionally used in conjunction with the process of the present invention, to hydrolyse an ester or as a polymer breaker, it is necessary to select an enzyme which remains active in the treatment fluid under reservoir conditions for at least as long as the catalytic activity is needed. It is generally advantageous for the enzymes to be readily water soluble although the enzymes may also be active and be used in low water activity environments or two-phase systems such as emulsions or dispersions.

Typically, isolated enzymes are used. Enzymes may be isolated from plant, animal, bacterial or fungal sources. The enzymes may be produced from wild-type, conventionally bred, mutated or genetically engineered organisms. The enzymes may, optionally, be chemically modified, as long as they retain or possess the desired catalytic ability. Preferably, the enzymes will be industrial enzymes available in bulk from commercial sources.

Each of components (i) and (ii) is contained in a treatment fluid in which it is dissolved or dispersed in water. The components may be contained either together in a single treatment fluid or in separate treatment fluids. If they are contained in separate treatment fluids, these fluids undergo mixing once they have been introduced into the reservoir. The or each treatment fluid is formulated outside the reservoir before being introduced downhole and is chosen to reflect the requirements of the treatment, such as amount of acid required, rate of production of acid required, type of breaker needed, chemical compatibility with the formation and the conditions of the reservoir, in particular the temperature.

When a single treatment fluid is used this is normally prepared by blending component (ii), either as a solid or in the form of a concentrated solution, with suitable water, for example city (drinking) water, fresh surface or well water, produced water or sea water. This forms a base fluid. Typically component (i) and, if required, any other components such as ester hydrolysing catalysts and/or polymer breakers are added to and mixed into the base fluid by suitable means. The treatment fluid may be prepared batchwise in tanks and other suitable vessels by adding component (i) to the base fluid with agitation and achieving thorough mixing by recirculating the treatment fluid through a blender such as a paddle blender for a suitable period of time.

In some circumstances, use of an emulsion of component (i) may be desirable. If batch-wise preparation is not possible or desirable (for example if a dispersion is used which is difficult to keep evenly dispersed in a large holding vessel), or if it is preferred the treatment fluid may be prepared by adding the individual components to the water on a continuous, preferably carefully controlled and monitored basis ("on the fly") while the treatment fluid is being injected into the underground reservoir. Suitable processes for preparing the chosen treatment fluid will be well known to those skilled in the art.

If desired, component (i) may comprise more than one ester where this is considered beneficial to the treatment. Similarly component (ii) may comprise more than one type of compound containing a carboxylate function.

It will be apparent that carboxylic acid salts already present downhole, for instance from the fluid used to drill the well, may contribute to the process of the present invention if there is sufficient mixing of fluids downhole to bring them into contact with the ester component (i)

The concentrations of components (i) and (ii) in the or each treatment fluid will be selected according to the requirements of the intended acidising treatment. Concentrations will typically be of the order of 1 to 20 % w/v of component (i) per litre of base fluid and 10 to 75% w/v of component (ii), although higher or lower concentrations may be appropriate in some situations. Optionally, where a treatment fluid additionally contains a polymer or gel breaker, the concentration of any polymer breaker will be selected such that polymers or gels present will be degraded within the desired period of time. Where enzymes are used, typical enzyme concentrations will be 0.05% to 5% v/v of commercial liquid enzyme preparations or about 0.005 to 0.5% v/v of dried enzyme preparation. Preferably liquid preparations of enzymes will be used for ease of handling.

In one embodiment of the process of the invention, the treatment fluid further includes one or more an ester hydrolysing enzyme or other non-enzyme ester-hydrolysing catalyst according to the methods of US 5,678.632 and WO 01/02698 that also serve to increase the rate of hydrolysis of the ester. In some embodiments of the present invention, one or more oxidant or enzyme polymer breakers may also be incorporated into the treatment fluids.

Polymer breakers, enzymes and non-enzyme catalysts may, if desired, also be used in the form of delayed release preparations, such as will be well known by those skilled in the art. Use of delayed release preparations may delay acidizing polymer

breaking in situations where this may be desirable, such as breaking of a filter cake over a long horizontal interval or where the treatment fluid is used as the carrier fluid for the gravel pack but where an intact filter cake is required during the process of placing the gravel.

The or each treatment fluid may also contain further chemical additives such as are commonly used in the treatment of underground formations, such as surfactants, mutual solvents, foaming and chelating agents if their inclusion is deemed to be beneficial and if they are sufficiently compatible with the other components of the treatment fluid and the formation fluids.

The or each treatment fluid is conveniently introduced into the underground formation via injection or production wells that extend into the reservoir. The wellbore may be vertical, deviated, inclined or horizontal. If being introduced into a newly drilled well, particularly if being used to remove damage caused during drilling, such as filter cakes, a treatment fluid may conveniently be introduced via the drill string. This may be achieved using the mud pumps. The corrosivity of a treatment fluid will be taken into account in deciding if it may be introduced into wells or the drill string without the need to add corrosion inhibitors. If required, suitable corrosion inhibitors may be added to treatment fluids. The or each treatment fluid will normally be introduced at below fracture pressure but may if desired be injected at above fracture pressure.

The acidising effect achieved *in situ* in a reservoir by the process of the present invention may be put to a number of different end uses. For instance, the process may be conducted such that, in step (b), acid is produced in an amount effective to dissolve acid soluble material in the reservoir, to increase the rate of productivity or injectivity of wells drilled into the formation, to treat filter cake, to treat filter cake following a gravel packing operation, to treat a biofilm, to break a pH sensitive cross-linked gel or to disrupt mixed metal hydroxides or complexes of mixed metal

hydroxides. When filter cake is treated, whether following a gravel packing operation or not, the acidising effect may bring about partial or complete removal of the filter cake.

The process of the present invention can be used to achieve near wellbore or fracture face damage removal, deep matrix acid stimulation or acidizing of induced or natural fractures, particularly in carbonate formations. Because the fluid is essentially non-reactive when placed, excellent zonal coverage can be achieved.

For near wellbore treatments, the volume of treatment fluid introduced into the reservoir will typically be at least equal to the wellbore volume plus an allowance for some leak off into the formation. A fluid volume of between 100% and 200% of the wellbore volume will normally be used although if a high rate of fluid loss is expected a volume up to 300% or higher of the well bore volume may be selected.

For treatments where the target is stimulation deeper into the formation such as within induced fractures or natural fractures or natural fracture networks a volume of treatment fluid will be selected appropriate to the requirements of the treatment. In one embodiment of the present invention, a volume of the treatment fluid which is sufficient to allow the fluid to penetrate up to several metres into a formation around a wellbore or behind a fracture face may be used. The production of acid *in-situ* can result in an increase in the matrix permeability of a carbonate formation to a depth up to several metres. Such treatments may be referred to as deep matrix stimulation. Using conventional acidizing it is extremely difficult to obtain a uniform effect. A much more uniform effect can be obtained using the process of the present invention.

Where damage is also removed from the near wellbore region or the fracture faces this will result in a negative skin which will increase the productivity of the well beyond that which can be achieved with even complete near wellbore damage removal. The volume of fluid needed for such treatments will depend on the porosity

of the formation, desired depth of penetration and dimensions of the wellbore and any fracture or fracture network. Acidizing several metres into the formation may also be effective for treating carbonate scaled sandstone reservoirs which also suffer from near wellbore damage.

In another embodiment of the process of the present invention, filter cake in gravel packing operations is treated. In such operations it is generally acknowledged that it is important to retain a filter cake during placement of the gravel pack. Following placement of the gravel pack, effective treatment, ideally the complete removal of the filter cake is required in order to ensure high productivity from the gravel packed well. A treatment fluid employed in the present process may be used as the base fluid used to place gravel for gravel packing operations or placed in the gravel packed well following the treatment. *In-situ* production of acid within the reservoir ensures that acid is delivered evenly to all parts of the gravel pack adjacent to the filter cake resulting in an even clean up of filter cake.

The well will normally be shut in after introduction of the or each treatment fluid for a period, typically between 2 hours and 2 weeks, preferably 24 hours to 1 week, to allow production of acid and if required breaking of polymer. The well is then put on or returned to production, or in the case of injection wells, put on injection. In some cases it may be desirable to leave the well shut in for a prolonged period of time, from several months to a year, following the treatment, before commencing production or water injection

It is also possible to introduce the or each treatment fluid into the reservoir via coiled tubing or via bullheading of the fluid.

The present invention has the following particular advantages. The process provides a simple, effective and convenient way to acidise underground formations using a single fluid. The process increases the rate of ester hydrolysis to achieve acidising

within a shorter and more acceptable period of time in situations where the rate of ester hydrolysis might not otherwise be fast enough. For example, a treatment that may otherwise take 4 days might be completed in 2 days. Shortening the time needed to carry out a treatment can save significant amounts of downtime and lost production.

The process also allows the successful incorporation of oxidant, or enzyme polymer breakers into a treatment fluid capable of delivering a high concentration of acid. Because the acid is present in a non-acidic precursor form, as component (i), the breakers are not inactivated, as many would be by contact with conventional acids, and the stability and/or activity of certain breakers may be enhanced by the prevailing pH of the treatment fluid. A combination of acid and polymer breakers can therefore be delivered in a single treatment to permit a joint attack on both acid soluble and polymer components of certain types of damage such as filter cakes. This avoids the need for two separate treatment stages to clean up each type of damage.

Also the process is generally a very low hazard process compared to previous processes aiming to achieve a substantive degree of acidising. The process typically uses high flash point esters as component (i) and compounds as component (ii) that are generally low hazard. There is generally no need for high pressure, high rate injection.

In addition, the components of the system are generally environmentally acceptable. Components (i) and (ii), as well as other components which may be incorporated into the treatment fluid such as enzymes and certain oxidant components, for instance percarbonates, are of low environmental impact.

The rate of ester hydrolysis is increased over a wide range of concentrations of component (ii). Some examples of component (ii), for instance salts such as

potassium formate, are already in common use as drilling and completion fluids. They possess a unique range of properties that make them highly suitable as a basis for drilling and completion fluids. They are biodegradable, non-toxic and non-hazardous, non-damaging to oil and gas reservoirs, stabilise shales, inhibit hydrates and are non-corrosive. In their existing applications they are already well understood and generally accepted by those skilled in the art

The ability to achieve acidizing in brines across a wide range of specific gravities is also useful. For example, calcium formate brines have specific gravities up to about 2.36 and when blended with caesium tungstate can have specific gravities as high as 3.0

The following Examples further illustrate the invention.

Method

The dissolution of calcium carbonate by treatment fluids of the present invention was measured using 50 ml volume capped polypropylene tubes containing 20 ml of treatment fluid and 2 grams of a 1:1 mixture of ground calcium carbonate of average diameter 5 microns and 50 microns (a typical size of calcium carbonate used in drilling fluids).

Ester was added to the carboxylic acid salt solution and incubated at the desired temperature for the desired period of time. Samples were taken, centrifuged at 13,000 rpm (approximately 10,000 x *g*) using a rotor 7500 3325 in an Heraeus Biofuge Pico microcentrifuge to separate particulate calcium carbonate. The soluble calcium concentration present in the supernatant was determined using a colorimetric assay method.

The pH of the supernatants was determined at room temperature (25 degrees C) on samples cooled to room temperature.

Example 1.

Treatment fluids comprising 10% w/v 1,2,3-propanetriol diacetate and different potassium formate concentrations were incubated in the presence of calcium carbonate at 25, 40, 50, 60 and 70 degrees C and the soluble calcium concentration in the supernatants was determined after 24, 48, 72 and 96 hours.

The results are shown in Table 1 and Table 2. It can be seen that the amount of calcium dissolved from the calcium carbonate by treatment fluids containing 10% w/v 1,2,3-propanetriol diacetate and potassium formate increased with temperature, time and the concentration of potassium formate.

In controls containing no 1,2,3-propanetriol diacetate the maximum concentration of soluble calcium observed was 7 mM. This indicates that the potassium formate alone was not dissolving calcium carbonate and it was the combination of the ester and potassium formate salt solution that was effective.

Dissolution of calcium was higher in all concentrations of potassium formate than in controls with the ester alone. This indicates that the rate of hydrolysis of the ester was faster in the presence of potassium formate. Soluble calcium levels were increasing even in treatment formulations at near neutral (pH 7+/- 0.5) see Table 2 indicating that the increased rate is due to the presence of the carboxylic acid salt rather than acid or alkali catalysed hydrolysis of the ester.

Example 2.

Treatment fluids comprising 10% w/v 1,2,3-propanetriol diacetate and either 30% w/v potassium formate or an equimolar concentration of sodium acetate were incubated in the presence of calcium carbonate at 60 and 70 degrees C. The soluble calcium concentration in the supernatants was determined after 24 and 44 hours.

The results are shown in Table 3. It can be seen that the amount of calcium dissolved from the calcium carbonate by treatment fluids containing 10% w/v 1,2,3-propanetriol diacetate and potassium formate or sodium acetate was very similar, indicating that equimolar solutions of the two carboxylic acid salts both increase the rate of hydrolysis of the ester to a similar degree. In the absence of 10% w/v 1,2,3-propanetriol diacetate dissolution of calcium carbonate was very low (maximum of 1 mM). Dissolution of calcium was higher in the treatment fluids containing either carboxylic acid salt than in controls with the ester alone.

Table 1. Soluble calcium levels in supernatant in treatment fluids containing 10% w/v 1,2,3-propanetriol diacetate in contact with ground calcium carbonate at 24,48,72 and 96 hours at different temperatures and potassium formate concentrations.

| Temperature °C | Potassium formate concentration (weight/volume) | Soluble Calcium (mM) | | | |
|---|---|---|---|---|---|
| | | 24 hours | 48 hours | 72 hours | 96 hours |
| 25 | 0% | 3 | 4 | 2 | 9 |
| 25 | 15% | 5 | 8 | 7 | 11 |
| 25 | 30% | 7 | 9 | 8 | 14 |
| 25 | 45% | 9 | 13 | 13 | 18 |

| | | | | | |
|---|---|---|---|---|---|
| 25 | 60% | 12 | 17 | 19 | 26 |
| 25 | 75% | 15 | 23 | 25 | 33 |
| | | | | | |
| 40 | 0% | 7 | 13 | 16 | 17 |
| 40 | 15% | 12 | 19 | 26 | 35 |
| 40 | 30% | 16 | 23 | 30 | 36 |
| 40 | 45% | 23 | 33 | 42 | 50 |
| 40 | 60% | 31 | 43 | 57 | 69 |
| 40 | 75% | 42 | 59 | 76 | 91 |
| | | | | | |
| 50 | 0% | 10 | 15 | 23 | 30 |
| 50 | 15% | 22 | 32 | 49 | 60 |
| 50 | 30% | 23 | 40 | 53 | 65 |
| 50 | 45% | 37 | 31 | 68 | 79 |
| 50 | 60% | 44 | 67 | 90 | 103 |
| 50 | 75% | 53 | 80 | 104 | 119 |
| | | | | | |
| 60 | 0% | 21 | 23 | 36 | 52 |
| 60 | 15% | 45 | 54 | 77 | 104 |
| 60 | 30% | 43 | 59 | 81 | 104 |
| 60 | 45% | 50 | 76 | 99 | 118 |
| 60 | 60% | 57 | 96 | 121 | 145 |
| 60 | 75% | 68 | 111 | 141 | 162 |
| | | | | | |
| 70 | 0% | 23 | 49 | 77 | 102 |
| 70 | 15% | 53 | 105 | 143 | 188 |
| 70 | 30% | 61 | 117 | 153 | 200 |
| 70 | 45% | 78 | 130 | 162 | 198 |

| | | | | | |
|---|---|---|---|---|---|
| 70 | 60% | 90 | 151 | 180 | 217 |
| 70 | 75% | 96 | 164 | 203 | - |

Table 2. pH of supernatant in treatment fluids containing 10% w/v 1,2,3-propanetriol diacetate in contact with ground calcium carbonate at 24,48,72 and 96 hours at different temperatures and potassium formate concentrations.

| Temperature °C | Potassium formate concentration (weight/volume) | pH | | | |
|---|---|---|---|---|---|
| | | 24 hours | 48 hours | 72 hours | 96 hours |
| | | | | | |
| 25 | 0% | 6.70 | 6.86 | 6.90 | 6.77 |
| 25 | 15% | 7.65 | 7.45 | 7.41 | 7.32 |
| 25 | 30% | 8.16 | 7.99 | 7.91 | 7.80 |
| 25 | 45% | 8.88 | 8.68 | 8.56 | 8.44 |
| 25 | 60% | 9.66 | 9.46 | 9.29 | 9.17 |
| 25 | 75% | 10.31 | 10.16 | 9.97 | 9.82 |
| | | | | | |
| 40 | 0% | 6.56 | 6.39 | 6.48 | 6.12 |
| 40 | 15% | 7.13 | 6.95 | 7.01 | 6.82 |
| 40 | 30% | 7.60 | 7.42 | 7.45 | 7.27 |
| 40 | 45% | 8.29 | 8.07 | 8.05 | 7.84 |
| 40 | 60% | 9.10 | 8.86 | 8.78 | 8.54 |
| 40 | 75% | 9.85 | 9.62 | 9.51 | 9.27 |
| | | | | | |
| 50 | 0% | 6.45 | 6.20 | 6.17 | 6.01 |

| | | | | | |
|---|---|---|---|---|---|
| 50 | 15% | 6.85 | 6.74 | 6.77 | 6.58 |
| 50 | 30% | 7.33 | 7.20 | 7.17 | 7.01 |
| 50 | 45% | 8.04 | 7.84 | 7.76 | 7.58 |
| 50 | 60% | 8.87 | 8.63 | 8.48 | 8.25 |
| 50 | 75% | 9.63 | 9.38 | 9.25 | 9.00 |
| | | | | | |
| 60 | 0% | 6.27 | 6.10 | 6.00 | 5.78 |
| 60 | 15% | 6.65 | 6.58 | 6.54 | 6.48 |
| 60 | 30% | 7.11 | 7.00 | 6.96 | 6.89 |
| 60 | 45% | 7.79 | 7.64 | 7.55 | 7.47 |
| 60 | 60% | 8.62 | 8.38 | 8.23 | 8.09 |
| 60 | 75% | 9.39 | 9.17 | 9.00 | 8.79 |
| | | | | | |
| 70 | 0% | 6.10 | 5.84 | 5.89 | 5.66 |
| 70 | 15% | 6.43 | 6.41 | 6.34 | 6.28 |
| 70 | 30% | 6.89 | 6.84 | 6.81 | 6.72 |
| 70 | 45% | 7.52 | 7.41 | 7.42 | 7.33 |
| 70 | 60% | 8.33 | 8.09 | 8.01 | 7.88 |
| 70 | 75% | 9.18 | 8.85 | 8.69 | 8.47 |

Table 3. Soluble calcium concentrations and pH of supernatants measured in treatment fluids containing 10% w/v 1,2,3-propanetriol diacetate and either water (control) 30% potassium formate or an equimolar concentration of sodium acetate. Treatment fluids were in contact with ground calcium carbonate at 24 and 48 hours at 60 and 70 degrees C.

| Temp 60°C | | 24 hours | | 44 hours | |
|---|---|---|---|---|---|
| | | Soluble calcium (mM) | pH | Soluble calcium (mM) | pH |
| | Water plus ester (control) | 13 | 6.31 | 25 | 6.02 |
| | 30% potassium formate | 43 | 7.02 | 61 | 7.04 |
| | Sodium acetate* | 37 | 6.51 | 56 | 6.46 |
| Temp 70° C | | | | | |
| | Water plus ester (control) | 20 | 5.89 | 38 | 5.80 |
| | 30% potassium formate | 65 | 6.77 | 102 | 6.81 |
| | Sodium acetate* | 62 | 6.33 | 101 | 6.21 |

* equimolar to 30% potassium acetate

Example 3.

Treatment fluids comprising 10% w/v 1,2,3-propanetriol diacetate and 22.5% w/v ammonium formate (equimolar to 30% w/v potassium formate) were incubated in the presence of calcium carbonate at 60 and 70 degrees C. The soluble calcium concentration in the supernatants and the pH was determined after 24, 48 and 72 hours.

The results are shown in Table 4. It can be seen that soluble calcium was again released from the calcium carbonate by the treatment fluid. Calcium release was similar to or greater to that released by potassium formate or sodium acetate used in the previous examples. The results indicate that ammonium formate is also effective at increasing the rate of hydrolysis of esters.

Table 4. Soluble calcium concentrations and pH of supernatants measured in treatment fluids containing 10% w/v 1,2,3-propanetriol diacetate and either water (control) or 22.5% ammonium formate. Soluble calcium measured at 24, 48 and 72 hours, incubations at 60 and 70 degrees C.

| Temp 60°C | | 24 hours | | 48 hours | | 72 hours | |
|---|---|---|---|---|---|---|---|
| | | Soluble calcium (mM) | pH | Soluble calcium (mM) | pH | Soluble calcium (mM) | pH |
| | Water plus ester (control) | 26 | 7.28 | 28 | 7.33 | 32 | 7.46 |
| | Ester plus 22.5 % w/v ammonium formate | 70 | 6.13 | 111 | 5.99 | 158 | 5.99 |
| Temp 70°C | | 24 hours | | 48 hours | | 72 hours | |
| | | Soluble calcium (mM) | pH | Soluble calcium (mM) | pH | Soluble calcium (mM) | PH |
| | Water plus ester (control) | 32 | 7.36 | 38 | 7.48 | 42 | 7.61 |
| | Ester plus 22.5 % w/v ammonium formate | 110 | 5.91 | 176 | 5.75 | 238 | 5.80 |

## CLAIMS

1. A process for treating an underground reservoir, which process comprises
   (a) introducing into the reservoir, separately or together:
      (i) an ester, and
      (ii) a compound containing at least one carboxylate functionality, the compound being water-soluble and capable of increasing the rate of hydrolysis of the ester;
   each of components (i) and (ii) being contained in a treatment fluid in which it is dissolved or dispersed in water; and
   (b) allowing the ester to hydrolyse to produce an organic acid in an amount effective to acidise the underground reservoir.

2. A process according to claim 1 wherein components (i) and (ii) are contained in a single treatment fluid.

3. A process according to claim 1 or 2 which further comprises introducing into the reservoir a polymer breaker component (iii) in an amount effective to degrade polymers present within the reservoir.

4. A process according to any one of the preceding claims wherein the underground reservoir is a hydrocarbon reservoir.

5. A process according to claim 4 which further comprises recovering a hydrocarbon from the treated reservoir.

6. A process according to claim 4 or 5 wherein the hydrocarbon is oil.

7. A process according to claim 4 or 5 wherein the hydrocarbon is a gas.

8. A process according to any one of claims 1 to 3 wherein the underground reservoir is a water reservoir.

9. A process according to claim 8 which further comprises recovering water from the treated reservoir.

10. A process according to any one of the preceding claims wherein component (ii) is a salt of an aliphatic carboxylic acid of formula $RCO_2H$ wherein R is selected from hydrogen, an alkyl group having from 1 to 6 carbon atoms and $-R'-CO_2H$ wherein R' is a bond or an alkylene group having from 1 to 6 carbon atoms, the said alkyl or alkylene group being branched or unbranched and unsubstituted or substituted.

11. A process according to any one of the preceding claims wherein component (ii) is a salt of formic acid or acetic acid.

12. A process according to claim 11 wherein the salt of formic acid or acetic acid is a salt with a metal of Group I or Group II of the Periodic Table.

13. A process according to claim 11 wherein the salt of formic acid or acetic acid is an ammonium salt.

14. A process according to any one of claims 1 to 11 wherein component (ii) is ammonium acetate, ammonium formate, potassium acetate, potassium formate, sodium acetate, sodium formate, caesium formate, caesium acetate, calcium acetate, calcium formate, magnesium acetate or magnesium formate.

15. A process according to any one of the preceding claims wherein the ester is a carboxylic acid ester

16. A process according to any one of the preceding claims wherein the ester is an ester of an aliphatic carboxylic acid of formula $RCO_2H$ wherein R is selected from hydrogen, an alkyl group having from 1 to 6 carbon atoms and $-R'-CO_2H$ where R' is a bond or an alkylene group having from 1 to 6 carbon atoms, the said alkyl or alkylene group being branched or unbranched and unsubstituted or substituted

17. A process according to any one of the preceding claims wherein the ester is a carboxylic acid ester of 1,2,3-propanetriol , ethylene glycol , diethylene glycol or triethylene glycol .

18. A process according to any one of the preceding claims wherein the ester is an ester of acetic acid or formic acid with 1,2,3-propanetriol, ethylene glycol, diethylene glycol or triethylene glycol .

19. A process according to claim 3 wherein the polymer breaker is an enzyme

20. A process according to claim 19 wherein the polymer breaker is an enzyme which can degrade starch, xanthan, cellulose, guar, scleroglucan or succinoglycan, or derivatives of these polymers.

21. A process according to claim 3 wherein the polymer breaker is an oxidant.

22. A process according to claim 21 wherein the polymer breaker is a persulphate, hypochlorite, peroxide, perborate, percarbonate, perphosphate, persilicate, a metal cation or a hydrogen peroxide adduct.

23. A process according to claim 22 wherein the hydrogen peroxide adduct is urea hydrogen peroxide or magnesium peroxide.

24. A process according to any one of the preceding claims which further comprise introducing into the reservoir a peroxide to generate a peracid polymer breaker *in situ*.

25. A process according to any one of the preceding claims wherein the or each treatment fluid is introduced into the reservoir via a wellbore which extends to the reservoir.

26. A process according to claim 25 wherein the wellbore is vertical, deviated, inclined or horizontal.

27. A process according to any one of claims 1 to 24 wherein the or each treatment fluid is introduced into the reservoir via the drillstring.

28. A process according to any one of claims 1 to 24 wherein the or each treatment fluid is introduced into the reservoir via coiled tubing.

29. A process according to any one of claims 1 to 24 wherein the or each treatment fluid is introduced into the reservoir via bullheading of the fluid.

30. A process according to any one of claims 1 to 24 wherein the or each treatment fluid is used as the base fluid for a gravel packing operation.

31. A process according to any one of the preceding claims wherein at least one of the components is present in the form of a delayed release preparation.

32. A process according to any one of the preceding claims which comprises introducing the or each treatment fluid into the reservoir by injecting it at a rate below

the reservoir fracture pressure.

33. A process according to any one of claims 1 to 33 which comprises introducing the or each treatment fluid into the reservoir by injecting it at a rate above the reservoir fracture pressure.

34. A process according to any one of the preceding claims wherein, in step (b), acid is produced in an amount effective to dissolve acid soluble material in the reservoir.

35. A process according to any one of claims 1 to 33 wherein, in step (b), acid is produced in an amount effective to increase the rate of production or injectivity of wells drilled into the formation.

36. A process according to any one of claims 1 to 33 wherein, in step (b), acid is produced in an amount effective to increase the permeability of the formation.

37. A process according to any one of claims 1 to 33 wherein, in step (b), acid is produced in an amount effective to treat filter cake.

38. A process according to any one of claims 1 to 33 wherein, in step (b), acid is produced in an amount effective to treat filter cake following a gravel packing operation.

39. A process according any one of claims 1 to 33 wherein, in step (b), acid is produced in an amount effective to treat a biofilm.

40. A process according any one of claims 1 to 33 wherein, in step (b), acid is produced in an amount effective to break a pH sensitive cross-linked gel.

41. A process according to any one of claims 1 to 33 wherein, in step (b), acid is produced in an amount effective to disrupt mixed metal hydroxides or complexes of mixed metal hydroxides.

42. A process according any one of claims 1 to 33 wherein, in step (b), acid is produced in an amount effective to treat an induced or natural fracture or a natural fracture network.

43. A process according to any one of the preceding claims which further comprises introducing into the reservoir an enzyme or non-enzyme catalyst in an amount effective to increase the rate of hydrolysis of the ester.

44. A process according to any one of the preceding claims wherein component (ii) is present in whole or in part in the fluid used for drilling or workovers of the underground formation.

# INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 03/03038

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 E21B43/27

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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